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hereby declare that I am conversant with the English and
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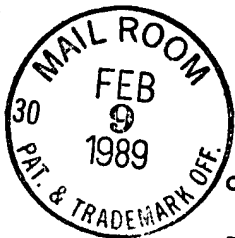
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A handwritten signature in dark ink, appearing to read 'W. G. Barb', written in a cursive style.

W. G. BARB

Improvement in the stabilization of halogenated vinyl
resins.



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The invention revealed in the following description concerns the stabilization to heat of halogenated vinyl resins; it more particularly concerns an improvement in stabilization achieved by the addition of tin derivatives. The invention particularly relates to adjuvants which, in conjunction with the tin compounds, render the resins more resistant to heat and to impact, and also more stable to light; it also comprises a process for the preparation of these adjuvants.

Given the considerable importance of vinyl resins, especially the polyvinyl chloride resins, stabilization of these resins has been the object of much work. It was indeed necessary to prevent the harmful effects of heating on halogenated vinyl polymers, so as to be able safely to subject these plastics to the various heat-forming processes. Stabilization by the addition of various tin compounds is well known, and has given rise to an abundant literature. The compounds that have proved very satisfactory are organic derivatives containing both tin and sulfur; nevertheless, as they do not allow the Sn/S ratio to be varied according to needs, there is a tendency for them to be replaced by mixtures of tin compounds with organic adjuvants, usually containing sulfur. Thus, a number of systems have been proposed comprising a mixture of one or more tin compounds with mercapto or thio compounds. For example, according to German Patent 1 217 609, the stabilizer consists of a mixture of mono- or di-organo tin with a

mercapto ester; US Patent 3 063 963 uses a mercapto acid or a mercapto alcohol with a di-organo tin compound; in accordance with US Patent 3 297 629, these compounds are replaced by a thio ether. Other patents describe the addition of substances such as aliphatic thio anhydrides, mercaptols, mercaptals, mercaptans, or organic disulfides. In a general way, according to the prior art, when the adjuvant contains a mercaptan function, the sulfur atom is always to be found in the acid residue, i.e. in the chain linked to the carbon atom of the carboxyl group.

Now, the different systems proposed hitherto present drawbacks either due to their insufficient effectiveness, as in the case of sulfides or disulfides, or to their unduly strong smell as occurs with thioglycolic acid esters, mercapto alcohols and the like, or because of the high cost of the products used, particularly in the case of thio acid anhydrides.

The present invention is the result of the unexpected observation that the abovementioned drawbacks can be removed, and that excellent stabilization of halogen-containing resins, particularly halogenated vinyl resins, can be achieved by the application of certain adjuvants, which differ from those whose use has been suggested hitherto. The applicants have found that it is possible, at a sufficiently low cost price, to obtain sulfurated esters which are very effective when used in conjunction with tin compounds, and which exude no smell;

moreover, these new adjuvants have a more favorable effect on the resin's viscosity at operating temperatures than other known stabilizing systems. They also allow good product lubrication during working, by facilitating slipping in the resin.

The halogen-containing resins to which the invention applies may be homopolymers such as, for example, polyvinyl chloride, polyvinylidene chloride, polychlorotrifluoroethylene, polytetrafluoroethylene, polychloroether, polydichlorostyrene, etc., copolymers such as polyvinyl acetochloride or the like, or various combinations or mixtures, for example polyvinyl chlorides modified with ethylene and/or propylene, with acrylonitrile-butadienestyrene, or ethylene-vinyl acetate and similar combinations.

The new adjuvants according to the invention are alkyl organic esters in which the alcohol residue of the ester contains a mercapto group. These compounds can be represented by the general formula:



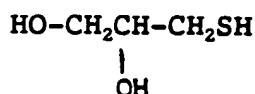
wherein R is a linear or branched alkyl or alkenyl, aryl or aralkyl, containing at least two carbon atoms, preferably 6 to 38 and most preferably 8 to 18, this radical moreover optionally carrying a second carboxyl group, which may or may not be combined with a second -R'SH grouping; R' designates a C_2 to C_{18} , more particularly C_2 to C_6 , alkylene radical, it being possible for this alkylene advantageously to carry one or more -OH groups.

Thus, contrary to the various mercapto esters of the prior art in which the -SH function is in the acid residue, i.e. in the chain corresponding to the R in the above formula, the products according to the invention are characterized in that they have their mercapto group in the alcohol residue, i.e. in the R' chain. It is surprising that, due to this difference in the position of the -SH group, the activity of the ester with regard to tin-based stabilizers is profoundly modified, to the point of removing the drawbacks noted above and achieving remarkable effectiveness. To this may be added the advantages of the ease of preparation and purification of these substances, and also the absence of smell.

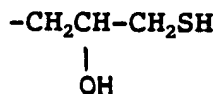
Although the R radical, in the esters according to the invention, may practically belong to any aliphatic mono- or diacid, the preferred esters are derived from fatty acids, particularly caprylic, pelargonic, capric, undecanoic, lauric, myristic, palmitic, stearic, iso-stearic, or from a mixture of such acids; thus, excellent stabilizers are obtained by associating a mixture of palmitic and stearic esters of an alkylene mercaptan with a tin-based stabilizer of known type. Also suitable are aryl acid esters, for example benzoic, benzylic, phenylacetic, phenylpropionic, etc.

As mentioned above, according to the invention, the ester may be a mono- or di-ester of a carboxylic diacid; suitable esters are, for example, those of succinic, adipic, dioleic, phthalic acids, etc.

The alcohol residue which, according to the invention, is a mercapto alcohol, may be derived from various mono- or polyalcohols having a thiol group, for example



these examples being in no way limiting. In practice, for economic reasons, mercaptoethyl and thioglycerol esters are particularly suitable, i.e. esters in which the -R'SH group is respectively



The higher the molecular mass of the ester, the lower the vapor pressure of this compound, which diminishes any risk of smell.

The use of the esters according to the invention in conjunction with tin compounds enables the required quantity of the latter to be very markedly reduced, which constitutes an appreciable economy; this economy may range from 20 up to 95% of the quantity of tin required in relation to the stabilization achieved with tin compounds alone.

The new adjuvants enable the coloration of the resins during heating to be reduced; they also enable the increase in viscosity caused by the addition of tin-based

stabilizers to be counteracted; these two effects can be obtained simultaneously. This is an important advantage, all the more so since the known tin-based stabilizers are not generally capable of producing these two effects together; some of them are mainly effective for reducing coloration and others for regulating viscosity. It is remarkable that these results can be obtained as much with mono- or di-organic tin derivatives, as with sulfur-free tin salts, as with sulfur-containing tin salts, or with mixtures of these.

The new adjuvants may be incorporated into the resin after polymerisation, but before the polymer has been dried, or at the time the polymer is used; their proportion may vary between wide limits, in particular from 0.1 to 5% by weight of the resin, and mainly between 0.5 and 2%.

The new adjuvants may be prepared by the direct action of an aliphatic acid on a mercapto alkanol, in the presence of an acid, in a hydrocarbon serving as solvent.

The invention is illustrated, though in no way limited, by the following examples.

EXAMPLE 1

Synthesis of mercaptoethyl stearate $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{CH}_2\text{CH}_2\text{SH}$

284 g, i.e. 1 mole, of stearic acid, 86 g, 1.1 mole, of 2-mercaptoethanol, 0.8 g of p-toluene-sulfonic acid and 200 ml of benzene are placed in a 1 l round-bottomed flask, equipped with a stirrer, a DEANSTARK (sic) separator and a cooler. The mixture is heated under nitrogen

until a good reflux is established, without allowing the temperature in the liquid to exceed 100°.

Heating under reflux is continued for about 6 h, to esterify the stearic acid. 200 ml of benzene are then added to the reaction medium; after cooling, this is washed twice using 100 ml of water each time.

The benzene is evaporated under reduced pressure, leaving 330 g of crude mercaptoethyl stearate ester; the latter assays at 9.2% SH as against the theoretical 9.6.

EXAMPLE 2

Synthesis of 3-thioglyceryl myristate $\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH}_2\text{CH}_2\text{-SH}$

The operating procedure of Example 1 is followed using 228 g, i.e. 1 mole, of myristic acid to which are added 216 g, i.e. 2 moles, of thioglycerol, 2 g of p-toluenesulfonic acid and 500 ml of benzene.

Esterification is stopped as soon as one mole of water has been recovered. The reaction medium is then washed three times with 500 ml of water. After evaporation of the benzene under pressure, 322 g of a crude 3-thioglyceryl myristate ester are collected, assaying at 8.4% SH as against the theoretical 10.4%.

EXAMPLES 3 to 6

In these examples, samples of polyvinyl chloride, stabilized with the adjuvant according to the invention, are tested with regard to coloration on heating. To this end, a composition comprising:

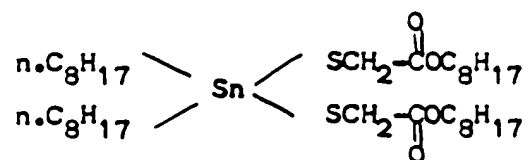
100 parts by weight of polyvinyl chloride, known by the trade name LACQVYL S071S, having a coefficient of

100 parts by weight of polyvinyl chloride, known by the trade name LACQVYL S071S, having a coefficient of viscosity K=56

0.5 parts of wax "E", as external lubricant

x part of a stabilizer whose nature and quantities are indicated in each of the examples

is malaxated at 180°C in a roller mixer. The results obtained are compared with those obtained with the conventional stabilizer di-n-octyltin bis(isooctyl-mercaptoacetate), which is known to be effective.



Coloration of the resin is observed in each case, and the time in minutes to the beginning of coloration is noted, as well as the time to browning of the sample.

In each example in this group, a table of results is given in which the proportions of stabilizer and adjuvant are indicated as percentages by weight relative to polyvinyl chloride; two other columns indicate the abovementioned coloration times.

EXAMPLE 3

The tests are carried out on the one hand with different proportions of the conventional stabilizer, whose formula is given above, and on the other hand with this same stabilizer in conjunction with mercaptoethyl

stearate described in Example 1.

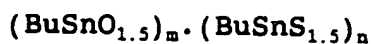
The following results are recorded.

	<u>Coloration</u>		
	<u>%</u>	<u>Beginning</u>	<u>Browning</u>
Tin-based stabilizer only	0.07	2'	5'
	0.25	4'	9'
	0.35	7'	12'
	0.70	11'	25'
Same stabilizer	0.07)		
+ mercapto-ethyl stearate	1.00)	4'	9'

Adding 1% stearate to the polyvinyl chloride is seen to achieve the same reduction in coloration at 180° in the presence of only 0.07% of conventional stabilizer as would have been obtained using 0.25% of the latter alone. This consequently results in a 72% economy of the costly tin-based stabilizer, whereas mercaptoethyl stearate is a very cheap substance. This economy is even greater in industrial cases where 1% or even larger proportions of tin-based stabilizer are used.

EXAMPLE 4

The conventional stabilizer tested here is a condensation polymer of butylstannoic and butylthiostannoic acids that may be represented by the formula



<u>Coloration</u>			
	<u>%</u>	<u>Beginning</u>	<u>Browning</u>
Tin-based stabilizer alone	0.1	8'	12'
" " " "	0.02	4'	6'
Same stabilizer	0.1)		
+ mercapto-ethanol stearate	1.00)	16'	25'
Same stabilizer +	0.02)		
same stearate	1.00)	7'	12'
Stearate alone	1.2	immediate	3'

These results show the very marked effect of mercapto-ethyl stearate in retarding coloration. Thus, with 1% stearate, the use of 0.02% of tin-based stabilizer is enough to achieve as good a performance as with 0.1% of the latter; use of the stearate according to the invention thus achieves a gain of 80% of the tin used.

The last horizontal line in the table shows that the effect of the added ester must be due to an unexpected synergic phenomenon, since mercaptoethyl stearate alone has no retarding action on the coloration of polyvinyl chloride in the heated state.

EXAMPLE 5

The conventional stabilizer tested is butylstannoic acid BuSnO_2H and the added stearate is the same as in the previous examples.

<u>Coloration</u>			
	<u>%</u>	<u>Beginning</u>	<u>Browning</u>
BuSnO_2H	0.05	immediate	10'

" "	0.05)		
+ stearat	1.00)	12'	25'

In point of fact, with butylstannoic acid alone it is not possible to obtain as good a stabilization as is achieved in conjunction with the stearate. It is to be noted that this last result is equivalent to that which would be obtained with the isooctyl-mercaptoacetate stabilizer whose formula is given above, in a proportion of 0.7%; the addition of stearate thus achieves a gain of more than 75% on the weight of tin.

EXAMPLE 6

The same tin-based stabilizer as in Example 5 is tested in conjunction with 3-thioglyceryl myristate in proportions of 0.05% of the first and 1% of the second. Coloration begins after 5' and browning after 12'; the addition of myristate has thus brought about a very marked improvement, since butyl-stannoic acid alone allowed coloration to begin immediately and browning to occur after 10', as seen in Example 5.

As regards browning, the result using myristate is equivalent to that obtained using the tin-based stabilizer of Example 3 on its own, at a level of 0.35%.

EXAMPLES 7 to 9

These examples give an account of the favorable effects of the adjuvants according to the invention on the viscosity of polyvinyl chloride. The reported determinations are carried out using the known Brabender

apparatus, which is a rotational torque rheometer. This instrument records the evolution of the torque required to stir the resin at a given temperature, in relation to time (it is described, for example, in *Plastiques Modernes et Elastomères* (Modern Plastics and Elastomers, March 1975)).

The measurements are made on the polyvinyl chloride resin known by the trade name S 111, whose viscosity constant is $K=67$. Certain agents are added to the resin, in the following proportions:

Polyvinyl chloride	100 parts by weight
CaCO_3	3 " "
TiO_2	1 " "
Wax "E"	0.8 " "
Stabilizing system	in the proportions shown in the examples.

The determinations are carried out at 200°C with the mixer rotor turning at a speed of 60 rpm.

Graphs showing the torque in m.kg in relation to time in minutes, from the third minute, are given in the appended drawings.

Fig.1 is a Brabender diagram of a mixture of known tin-based stabilizers.

Fig.2 is a similar diagram, obtained with the stabilizers of Fig.1 to which has been added an adjuvant according to the invention.

Fig.3 is a Brabender diagram obtained with another conventional stabilizer alone and in conjunction with an

adjuvant according to th invention.

Fig.4 relates to a third stabilizer of known type.

EXAMPLE 7

The stabilizer of known type is a mixture of butyl-thio-stannoic acid anhydride with di-n-butyl tin bis(isodecyl-mercapto-acetate).

In the diagram of Fig.1, Brabender graph 1 was plotted with polyvinyl chloride containing 1.8% of the above-mentioned stabilizer mixture, while graph 2 corresponds to 0.9% of the same stabilizer. The three graphs in Figure 2 correspond to polyvinyl chloride containing the following percentages of the same conventional stabilizer, moreover containing mercaptoethyl stearate.

	<u>Stabilizer</u>	<u>Stearate</u>
Graph 3	0.9	1
" 4	0.9	2
" 5	0.45	2

The graphs relating to a mixture containing stearate, i.e. graphs 3 to 5, can be seen to show a systematically lower plateau - by approximately 15% - than graphs 1 and 2 which correspond to the conventional stabilizer alone. This means that the power required to work the resin is less when the latter contains an ester according to the invention; the resulting advantage is obvious: production rate can be increased.

Another result is that, with an equal tin content, the systems containing stearate (graphs 3 and 4) ar much

better as regards the shape and the length of the plateau of the recorded graphs. Thus, graph 4 presents as long a plateau as graph 1, which means that the system containing 0.9% of tin-based stabilizer and 2% of stearate (graph 4) is as good as that containing 1.8% of the same tin-based stabilizer alone (graph 1); the addition of stearate hence achieves a 50% economy on the quantity of tin used.

In the same way, graph 5 is far better than graph 2, which means that 0.45% of tin-based stabilizer with 2% of stearate gives better results than 0.9% of tin-based stabilizer alone.

On the other hand, graphs 3 and 5 can be seen to be equivalent, meaning that 0.9% of stabilizer with 1% of stearate (graph 3) can be replaced by 0.45% of tin-based stabilizer plus 2% of stearate (graph 5); hence, at the cost of an increase in the stearate content, an even greater economy of tin can be achieved. Moreover, these graphs 3 and 5 are not very different from graph 1, at 1.8% of tin-based stabilizer, which serves as a basis for comparison in the present study.

It must also be noted that the gelling times of mixtures according to the invention are similar to or shorter than those of compositions containing the known tin-based stabilizer alone.

EXAMPLE 8

The stabilizer of known type which serves as a basis for comparison in the tests illustrated in Figure 3 is

di-n.butyl-tin bis(isooctylmercapto acetate).

Graph 6 corresponds to polyvinyl chloride containing 2.2% of this butyltin derivative, while graph 7 relates to a similar test, but with only 1.1% of this stabilizer and 1% of mercaptoethyl stearate.

The two graphs are observed to be practically equivalent, which means that a 50% gain on the quantity of tin used can be achieved by the addition of 1% of stearate. It is moreover to be noted that graph 7, according to the invention, is more regular, which means in practice that the mixing is proceeding more effectively.

EXAMPLE 9

The measurements here are made on the polyvinyl chloride described above, containing a known stabilizer comprising a condensation polymer of butylstannoic and butylthiostannoic acids.



In Figure 4, Brabender graph 8 corresponds to polyvinyl chloride containing 0.37% of the above stabilizer alone. Graph 9 is that obtained with the same resin to which, as well as the 0.37% of this known tin-based stabilizer, 1% of mercapto-ethyl stearate has been added; graph 10 corresponds to 0.19% of tin-based stabilizer and 2% of stearate. The latter is seen to be the best of all, meaning that much better results can be obtained with about half the amount of tin-based stabilizer by adding enough stearate.

EXAMPLE 10

Analogous measurements to those in Example 7 were made with mercaptoethyl palmitate as adjuvant for the tin-based stabilizer instead of the corresponding stearate. The Brabender graphs then had the same shape as graphs 3 to 5 in Figure 2 and were quantitatively very close to them. Thus, with 1% of mercaptoethyl palmitate and 0.9% of tin-based stabilizer, a torque of 1.4 m.kg is observed at 20 minutes.

EXAMPLE 11

The palmitate of Example 10 being replaced by mercapto-ethyl myristate, the Brabender diagrams still have the same shape; at 20 minutes the torque is observed to be 1.35 m.kg.

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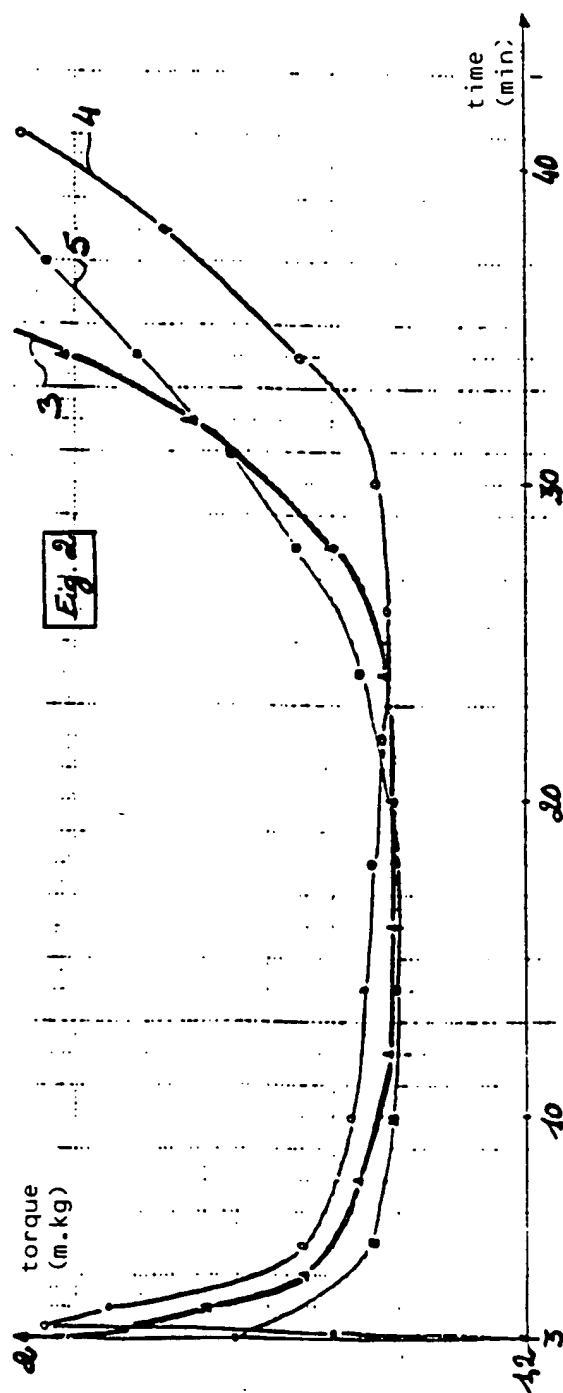
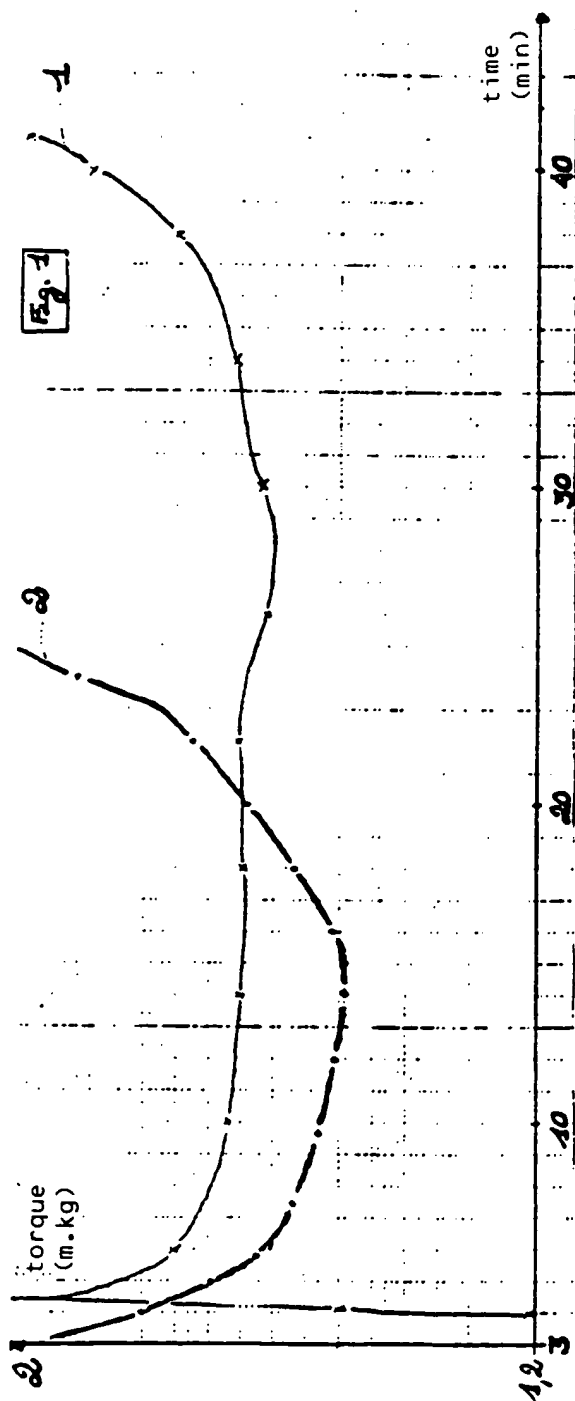
CLAIMS

1. Improvement in the stabilization of halogen-containing resins to heat, impact and light by the addition of tin compounds, which consists in moreover incorporating in the resin an organic adjuvant having a mercaptan function, characterized in that this adjuvant is an organic acid ester wherein the mercaptan function is linked to a carbon atom in the alcohol residue of this ester.
2. Improvement according to Claim 1, which consists in incorporating the ester adjuvant, containing a mercaptan function in the alcohol residue, in the resin stabilized with one or more tin compounds, characterized in that the proportion of this adjuvant is 0.1 to 5% and preferably 0.5 to 2% by weight of the resin.
3. Improvement according to Claim 2, characterized in that the adjuvant, which may comprise several esters, is added to the resin simultaneously with the tin compound or compounds, or separately.
4. Stabilization adjuvant, for achieving the improvement according to one of Claims 1 to 3, characterized in that it is of the type RCOO-R'SH where R is an alkyl or alkenyl containing at least 2 carbon atoms and preferably 8 to 18 C, or an aryl or aralkyl, this R optionally carrying a second carboxyl group or a second -COOR'SH grouping, while R' is a C_1 to C_{18} alkylene which may carry on or more -OH groups.

5. Adjuvant according to Claim 4, characterized in that RCOO- is a fatty acid residue, in particular caprylic, pelargonic, capric, undecanoic, lauric, myristic, palmitic or stearic.
6. Adjuvant according to Claim 4, characterized in that the grouping RCOO- belongs to an aliphatic diacid, in particular succinic, adipic or dioleic, or to an aromatic diacid, particularly phthalic.
7. Adjuvant according to one of Claims 4 to 6, characterized in that the -R'SH group is derived from a C_2 to C_6 mercapto-alkanol, in particular from: 1-mercapto-2-ethanol, 1-mercapto-3-propanol, 1-mercapto-2-hydroxy-3-propanol, or 1-mercapto-4-butanol.
8. Adjuvant according to one of Claims 4 to 7, characterized in that it is a mono-mercaptan.
9. Application of an adjuvant, according to one of Claims 4 to 8, to the stabilization of polyvinyl chloride or of a modified polyvinyl chloride, characterized in that it is achieved in accordance with one of Claims 1 to 3.

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PL. I-2



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